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G. Kok*, K. Darnall**, A. Winer**, J. Pitts**, and B. Cay.

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*Harvey Mudd College
Claremont, California 91711
**University of California
Riverside, California 92521

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Ambient Air Measurements of Hydrogen Peroxide in the California South Coast Air Basin

Gregory L. Kok*

Harvey Mudd College, Department of Chemistry, Claremont, Calif. 91711

Karen R. Darnall, Arthur M. Winer, and James N. Pitts, Jr.

Statewide Air Pollution Research Center, University of California, Riverside, Calif. 92521

Bruce W. Gay

U.S. Environmental Protection Agency, Research Triangle Park, N.C. 27711

■ Hydrogen peroxide (H_2O_2) concentrations were measured at two locations (Claremont and Riverside) in the California South Coast Air Basin during the months of July and August 1977. Three different analytical methods were employed: a chemiluminescent method and two colorimetric procedures. Typical midafternoon concentrations of H_2O_2 during moderate smog episodes (i.e., $O_3 \sim 150$–200 ppb) ranged from approximately 10 to 30 ppb. These values were significantly lower than those measured in a study in Riverside in 1970. In general, maximum H_2O_2 concentrations were observed at about the time of the ozone maximum, but in the course of a day H_2O_2 levels did not occur in a fixed ratio to O_3 concentrations, and in a number of cases the concentrations of H_2O_2 declined more slowly than those of ozone following the O_3 maximum. During this investigation signals corresponding to elevated levels of H_2O_2 (i.e., ~100 ppb) were observed by all three methods when grass or forest fire plumes impacted on the measurement site.

Hydrogen peroxide (H_2O_2) is expected to be a mechanistically significant species in photochemical smog as a chain terminator and as an index of hydroperoxyl radical (HO_2) concentrations (*1–3*). Thus, knowledge of the concentration of H_2O_2 in both polluted ambient atmospheres and in simulated atmospheric systems is of considerable interest, particularly to atmospheric modelers (*2–6*). However, due to the analytical difficulties encountered in measurements of part per billion (ppb) concentrations of H_2O_2, there have been relatively few laboratory or smog chamber studies in which H_2O_2 was monitored. In the laboratory studies H_2O_2 has been shown to be a product of the NO_x-photooxidation of formaldehyde (*1, 7, 8*) and of hydrocarbons (*9–11*). There has been only one set of atmospheric measurements, that of Bufalini et al. (*8, 9, 12*) in 1970. These workers reported H_2O_2 concentrations of up to 40 ppb in Hoboken, N.J., and of up to 180 ppb in Riverside, Calif.—in the latter case during a very severe smog episode in which the oxidant concentration reached 0.65 opm.

Until recently, only the wet chemical titanium sulfate ($TiSO_4$) colorimetric method of Purcell and Cohen (*7*) has been available for measurement of trace quantities of H_2O_2; with long-path infrared spectroscopy, H_2O and CH_4 interferences substantially raise the detection limits for H_2O_2. Recently, however, Kok et al. have developed a chemiluminescent method for the determination of H_2O_2 (*13*), and Pilz and Johann have put forward a titanium tetrachloride ($TiCl_4$) colorimetric method (*14*), which has been adapted (*15*) at the Statewide Air Pollution Research Center (SAPRC) of the University of California for chamber and ambient air measurements of low H_2O_2 concentrations.

We report here a joint investigation by workers from Harvey Mudd College, the UC-SAPRC and the Environmental Protection Agency (EPA) whose purpose was to obtain new measurements of H_2O_2 levels at receptor sites in the California South Coast Air Basin (SCAB) (in conjunction with the measurements of other pollutants) using three different methods of analysis. An unanticipated outcome of the present study was the observation of elevated H_2O_2 concentrations in wildfire plumes which impacted the sampling sites during ambient air monitoring.

Experimental

In an initial study, H_2O_2 measurements were made at the Harvey Mudd College campus at Claremont, Calif., using the luminol-based chemiluminescent method, which has been described in detail elsewhere (*13*). Briefly, the analytical system is based on the chemiluminescent oxidation of luminol by hydrogen peroxide in the presence of a metal catalyst. This reaction is carried out in a solution buffered to about pH 12. The reagents are metered by a peristaltic pump and mixed at the reaction cell. A high gain photomultiplier tube and associated electronics are used for measurement of the chemiluminescent light intensity. With this basic system a detection limit for hydrogen peroxide in the liquid phase of about 1 ppb is observed. Atmospheric H_2O_2 can be sampled by trapping the H_2O_2 in a midget impinger and analyzing the solution directly. In the present study sampling intervals were 15–20 min, and this gave a detection limit of approximately 0.4 ppb for gas phase H_2O_2.

A modification to the sampling system of the chemiluminescent H_2O_2 analyzer permits continuous determination of atmospheric H_2O_2. In place of the liquid sampling valve, a scrubbing coil is added to the sampling inlet of the basic chemiluminescent analyzer. Air and distilled water are continuously drawn through the coil, and the H_2O_2 is concentrated in the aqueous solution. The concentration of hydrogen peroxide in this solution is determined directly by the chemiluminescent analyzer. The sensitivity of this system for atmospheric H_2O_2 is approximately 1 ppb. Other atmospheric gases do not interfere significantly in the analysis for hydrogen peroxide with either of these analytical systems. In this study a glass and Teflon sampling system was used to bring outside air into the instrument laboratory. A Dasibi UV analyzer was used for the ozone measurements.

In Riverside, Calif., a series of measurements was made at the Statewide Air Pollution Research Center located on the University of California campus. In addition to measurements with the chemiluminescent method described above, H_2O_2 was monitored by two methods employing titanium salts, the Cohen and Purcell, $TiSO_4$–8-quinolinol, method, which has been described previously (*6, 8, 10, 12*), and a $TiCl_4$ method developed by Pilz and Johann (*14*) and modified by SAPRC workers (*15*).

Briefly, the $TiSO_4$–8-quinolinol method involves passing the air sample through a coarse fritted bubbler containing an aqueous $TiSO_4/(NH_4)_2SO_4/H_2SO_4$ solution at a concentration of ~50 $\mu g\ mL^{-1}$ of Ti(IV). After sampling, the pH of the so-

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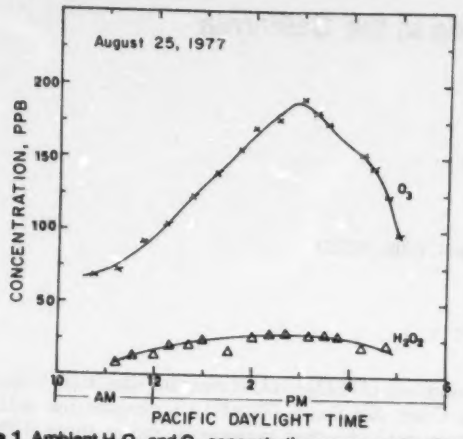

Figure 1. Ambient H_2O_2 and O_3 concentrations measured at Claremont, Calif.

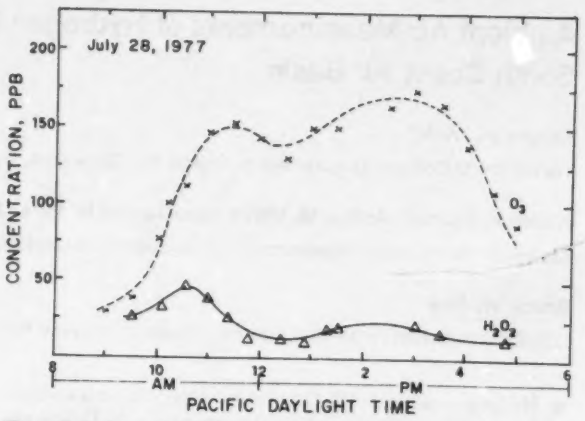

Figure 2. Ambient O_3 and H_2O_2 concentrations measured at Riverside, Calif.

lution is adjusted to 4.2 ± 0.2 using a sodium acetate buffer, and the mixture is then shaken with an aliquot of 0.1% 8-quinolinol in chloroform. The absorbance at 450 nm of the Ti(IV)–H_2O_2–8-quinolinol complex in chloroform is determined (a = 3060 M^{-1} cm^{-1}).

The $TiCl_4$ method involves sampling through a midget impinger containing an aqueous $TiCl_4$/HCl solution at a concentration of ~8 mg mL^{-1} of Ti(IV). A stable $TiCl_4$–H_2O_2 complex is formed immediately, and after dilution to a known volume, the absorbance of the complex at 410 nm is determined (a = 735 M^{-1} cm^{-1}). For H_2O_2 concentrations less than 100 ppb, 5-cm cells and a 0.05 A full-scale range were used. The principal difficulty encountered with this method was the formation of a fine precipitate, presumably consisting of either atmospheric particulates or TiO_2 formed in the solution. The presence of such precipitates contributes to scattering in the visible spectra with, as expected, the effect being more pronounced at shorter wavelengths. In the Riverside study NO and NO_2 were determined with a Bendix NO–NO_x analyzer, and O_3 measurements were made with a Dasibi UV analyzer.

Results and Discussion

Ambient Air Measurements. Measurements of H_2O_2 levels in the ambient atmosphere were made on July 19 and August 10 and 25, 1977, in Claremont, Calif., and in Riverside, Calif., during the week of July 25–29, 1977. Figures 1 and 2 show typical O_3 and H_2O_2 time-concentration profiles observed at Claremont and Riverside during the measurement periods. The majority of the H_2O_2 data reported here were gathered by the chemiluminescent method (*8*) since data points could either be recorded continuously or at 15–20-min intervals. The sampling periods for the $TiSO_4$ and $TiCl_4$ methods were from 40 to 60 min.

For the low ambient H_2O_2 concentrations encountered in this study, there were often significant differences between results obtained with the three analytical methods, although generally these were not greater than the combined uncertainties associated with the respective methods. In general, the data from the two colorimetric techniques were more erratic and usually somewhat lower than concentrations obtained with the chemiluminescent method. Table I compares data obtained by the different analytical methods for one monitoring period. The uncertainties for the concentrations of H_2O_2 observed are assigned as approximately ±5 ppb for the chemiluminescence method and ±8 and ±6 ppb for the $TiSO_4$ and the $TiCl_4$ methods, respectively. Of the two colorimetric methods the $TiCl_4$ procedure was experimentally most straightforward and appeared to provide more consistent data.

Differences between H_2O_2 concentrations obtained by the three methods (see Table I) are indicative of the substantial difficulties encountered attempting to quantitatively determine ambient concentrations H_2O_2 which were generally <20 ppb. Sampling and handling procedures were somewhat more difficult in the field measurements than in laboratory experiments, and in the case of the colorimetric methods, signal-to-noise ratios and/or signal-to-background (for example, due to scattering by particles) ratios were low. For these reasons any one H_2O_2 concentration reported here may be uncertain by as much as a factor of two. Thus, the major contribution of the present study is to definitively establish the *order of magnitude* of H_2O_2 concentrations in moderate to severe photochemical smog episodes at downwind receptor sites as being of the order 10–20 ppb, rather than 1–2 or 100–200 ppb. Thus, for the purposes of those modeling photochemical smog formation, a value for H_2O_2 concentrations of 20 ± 10 ppb for times near ozone maxima of ~0.15–0.35 ppm seems appropriate on the basis of the data obtained here.

H_2O_2 concentrations obtained in the present study are very substantially lower than those obtained in the earlier work of Bufalini et al. (*8, 10, 12*). For example, in the former study at

Table I. Comparison of H_2O_2 Measurements[a] by Three Different Analytical Techniques

$TiSO_4$[b]		$TiCl_4$[c]		chemiluminescent[d]	
period of measurement	H_2O_2 (ppb)	period of measurement	H_2O_2 (ppb)	period of measurement	H_2O_2 (ppb)
11:15–12:00	17	11:40–12:20	10	11:30–11:45	12
12:00–1:00	4	12:40–1:20	14	12:30–12:50	10
1:00–2:10	6	1:40–2:20	7	1:15–1:35	19
2:10–3:00	20	2:40–3:20	8	2:40–3:00	19

[a] Ambient air samples July 28, 1977. [b] Refs. *6* and *8*. [c] Refs. *14* and *15*. [d] Ref. *13*.

maximum oxidant concentrations of 0.6 and 0.3 ppm, H_2O_2 levels of 180 and 60 ppb, respectively, were reported. In contrast, on July 25 and 26, 1977, ozone concentrations reached approximately 0.3 ppm in Riverside, but H_2O_2 concentrations observed with the chemiluminescent method were between 25 and 30 ppb; whereas on July 28, O_3 peaked at approximately 0.2 ppm, but H_2O_2 concentrations were less than 20 ppb as measured by all three methods. These differences in concentrations of H_2O_2, relative to O_3 or oxidant, between the 1970 and 1977 studies are probably actually greater than indicated by the raw data cited, since in the earlier study oxidant rather than ozone was measured, and in the time between the two studies the calibration procedure in the Federal reference method for oxidant has been shown to result in oxidant measurements approximately 10–20% too high (*16, 17*).

Whether or not the apparent decline in ambient H_2O_2 concentrations between 1970 and 1977 is real is difficult, if not impossible, to establish. Recent long-path infrared measurements at SAPRC (*18, 19*) have shown that ambient HCHO concentrations during smog episodes in Riverside are low, in the range of 2–20 ppb. This is consistent with low H_2O_2 levels since formaldehyde is both a direct and indirect precursor of H_2O_2 via Reactions 1 and 3 shown below. These same infrared measurements have established an upper limit for H_2O_2 in Riverside ambient air of approximately 50 ppb (*20*), which is consistent with the chemiluminescent and titanium salt measurements in the sense that none of these exceeded 50 ppb.

An important conclusion from our simultaneous measurements of H_2O_2 and O_3 is that the H_2O_2 levels observed do not occur in a fixed ratio to O_3. Thus, in a number of cases the concentrations of H_2O_2 were observed to decline more slowly than those of O_3 following the O_3 maximum, and in some cases H_2O_2 concentrations remained essentially constant into the early evening hours (see Figure 3). This is consistent with the fact that major loss processes for H_2O_2 are photolysis (*21, 22*) and reactions with the hydroxyl radical (*23*) whose concentration tends toward zero after sunset (*24, 25*). To date no overnight studies have been conducted to obtain complete diurnal concentration-time profiles for H_2O_2.

H_2O_2 levels observed in the mornings tended to be in the range 5–10 ppb, although in several cases (see Figure 3) concentrations between 25 and 35 ppb were observed. It would be of considerable interest to determine H_2O_2 levels in the early morning prior to sunrise, since, if substantial H_2O_2 were present at this time, it would undergo photolysis to produce hydroxyl radicals which would accelerate the production of photochemical oxidant.

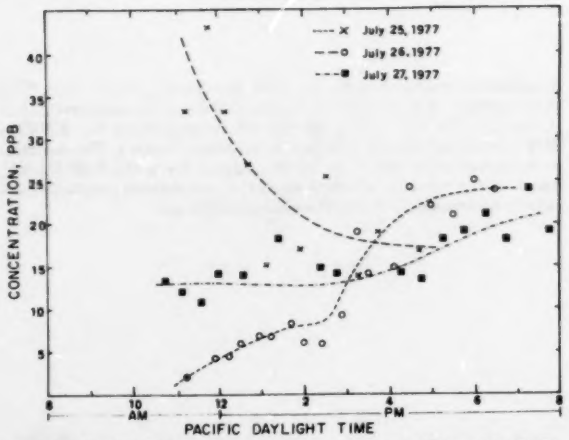

Figure 3. Ambient H_2O_2 concentrations measured at Riverside, Calif., on July 25–27

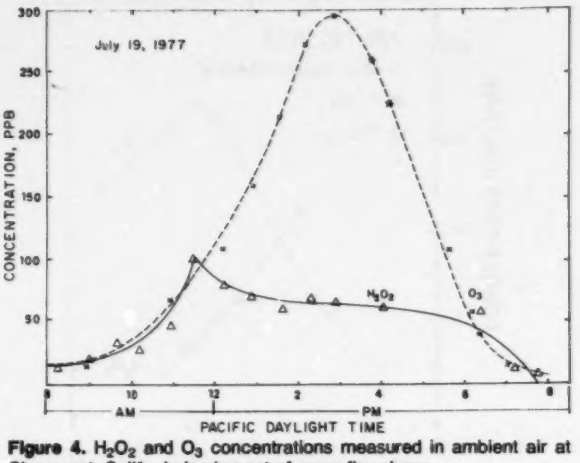

Figure 4. H_2O_2 and O_3 concentrations measured in ambient air at Claremont, Calif., during impact of grass fire plume

The mechanism of formation of H_2O_2 in NO_x–hydrocarbon photooxidation systems has been discussed in detail elsewhere (*3, 8*). Possible reactions leading to the production of H_2O_2 are

$$HO_2 + HCHO \rightarrow H_2O_2 + HCO \quad (1)$$

$$2HO_2 \rightarrow H_2O_2 + O_2 \quad (2)$$

with Reaction 2 probably being the more important since Reaction 1 is known to be slow (*26*). Thus, any source of H atoms for example

$$HCHO + h\nu \rightarrow H + HCO \quad (3)$$

can contribute to H_2O_2 formation via

$$H + O_2 + M \rightarrow HO_2 + M \quad (4)$$

Hydrogen Peroxide Concentrations in Fire Plumes. On two of the days for which H_2O_2 measurements were being made, wildfires were occurring directly upwind of the sampling sites. In the first of these cases (July 19), a small brush fire occurred approximately 6 miles west of the Claremont sampling site. The fire started at approximately 8:00 a.m. in the morning, and burned 3 acres before being extinguished at 12:30 p.m. H_2O_2 and O_3 data obtained for this day are shown in Figure 4. Hydrogen peroxide concentrations observed on this day were substantially higher than during any other monitoring period at Claremont. In particular, the H_2O_2 concentration reached a maximum of 100 ppb several hours before the O_3 maximum, observed at ~2:30 p.m. The H_2O_2 level decayed slowly from 11:30 on but remained high relative to H_2O_2 levels observed on other days.

On July 29 the plume from a wildfire in the Cleveland National Forest, located approximately 20 miles southwest of Riverside, was blown over the Riverside area. This fire had been burning out of control for approximately two days prior to the 29th. Results from the H_2O_2 and O_3 measurements for this day are shown in Figure 5.

The observation in both of these cases of relatively low levels of O_3 compared to H_2O_3 concentrations is of considerable interest, since it provides the clearest example of the deviation of H_2O_2 time-concentration profiles from those for O_3 or oxidant that has been reported to date. The occurrence of some unknown interference leading to these observations of elevated H_2O_2 levels cannot be definitively ruled out at this time; however, Kok et al. (*13*) have shown that their chemiluminescent method is not subject to interference by particles. Moreover, the good correlations obtained between the $TiCl_4$ method (an absorption technique) and the chemiluminescent

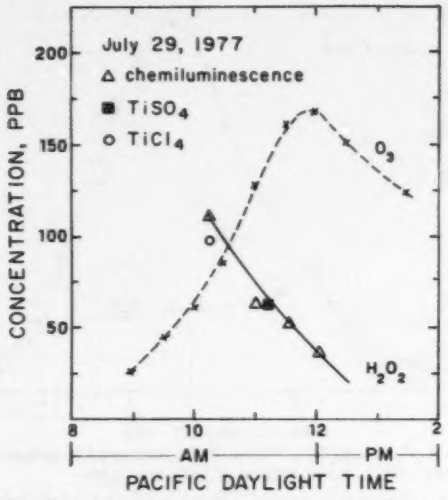

Figure 5. H_2O_2 and O_3 concentrations measured in ambient air at Riverside, Calif., on July 29, 1977, during impact of forest fire plume

method (a luminescence technique) suggest that elevated H_2O_2 levels are present in the fire plume.

Further support for concluding that the H_2O_2 measurements made here in wildfire plumes are not artifacts arises from cool flame combustion kinetics. At cool flame temperatures ($\lesssim$400 °C) the reaction R + O_2 produces HO_2 radicals and unsaturated products rather than RO_2 radicals (*27, 28*). The HO_2 becomes active in propagating chains via abstraction reactions of the type (*27, 28*)

$$RH + HO_2 \rightarrow H_2O_2 + R \qquad (5)$$

Unlike RO_2 radicals, HO_2 is thermally stable at cool flame temperatures, and hydrogen peroxide is likewise much more stable than organic hydroperoxides (*27, 28*). Thus, it appears quite plausible that the measurements we have obtained do in fact result from elevated concentrations of H_2O_2 produced during combustion in the wildfires whose plumes were sampled. To our knowledge this is the first such observation associated with wildfires, although recent attention has been given ther products formed in the burnings of forests (*29*).

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